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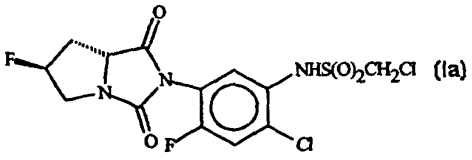
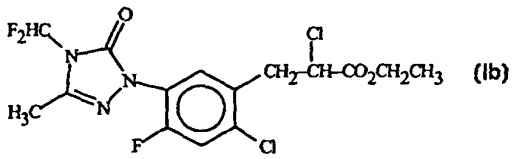
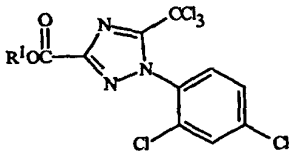


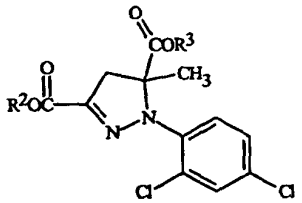
(Ia)



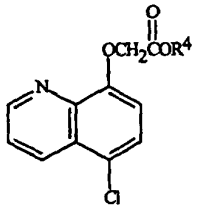
(Ib)



(IIa)



(IIb)



(IIc)

(57) Abstract

This invention relates to herbicidal mixtures of at least one compound selected from Formulae (Ia) and (Ib) with a safener selected from Formulae (IIa), (IIb) and (IIc) wherein R^1, R^2, R^3 and R^4 are as defined in the text, herbicidal compositions of said mixtures, and a method for the use of said mixtures to control undesired vegetation.

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TITLE

CROP-SAFENED HERBICIDAL MIXTURES

FIELD OF THE INVENTION

The present invention relates to mixtures of herbicides with safeners that reduce crop injury while retaining weed control.

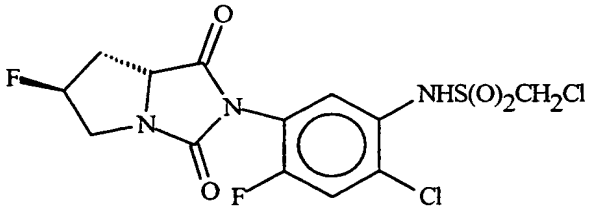
BACKGROUND OF THE INVENTION

The control of undesired vegetation is extremely important in achieving high crop efficiency. This can be achieved by the selective control of the growth of weeds in such useful crops as alfalfa, corn (maize), peanut (groundnut), potato, rape, rice, sorghum, soybean, sugar beet, tomato, vegetables, cool-season cereals including wheat, barley and rye, perennial plantation crops including banana, citrus, cocoa, coffee, grapes, hops, plantain, pineapple, oil palm, rubber, sugarcane, tea, fruit trees, nut trees and forests, and turf, among others. Unchecked weed growth in such useful crops can cause significant reduction in productivity and thereby result in increased costs to the consumers. The need for finding products that achieve such results continues to be commercially important.

Herbicidally active compounds are typically applied in combination with nonherbicidal formulating ingredients that facilitate application, increase wash-off resistance, improve penetration, etc. Certain rare combinations of herbicides with nonherbicidal compounds surprisingly reduce the herbicidal effect on crops while retaining useful weed control. The nonherbicidal compounds having this effect are termed "safeners" or "antidotes". By reducing crop injury while retaining control of weeds, effective weed-control selectivity is increased. Such valuable combinations have now been discovered.

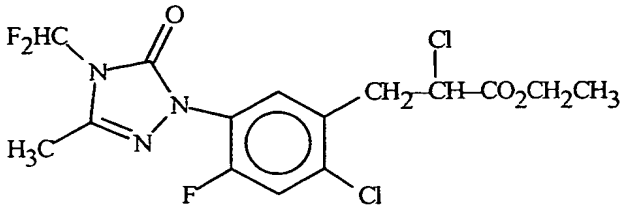
SUMMARY OF THE INVENTION

This invention relates to mixtures of chlorofluorobenzene herbicides with several compounds discovered to be useful safeners for these herbicides. The herbicidal mixtures comprise herbicidally effective amounts of at least one herbicidal compound selected from the group consisting of:



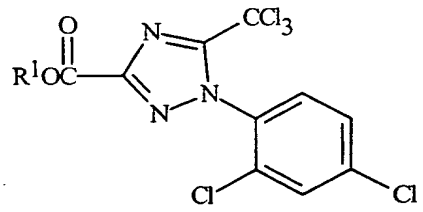
Ia

(6*S-cis*)-1-chloro-*N*-[2-chloro-4-fluoro-5-(6-fluorotetrahydro-1,3-dioxo-1*H*-pyrrolo-[1,2-*c*]imidazol-2(3*H*)-yl)phenyl]methanesulfonamide (**Ia**), or an agriculturally useful salt thereof; and



Ib

ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate (carfentrazone-ethyl, **Ib**), or an agriculturally useful salt thereof; in combination with an antidotally effective amount of a safener compound selected from the group consisting of:

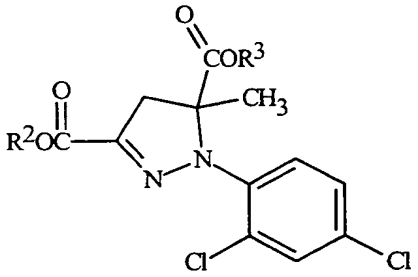


IIa

or an agriculturally useful salt thereof

wherein

R^1 is C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio;



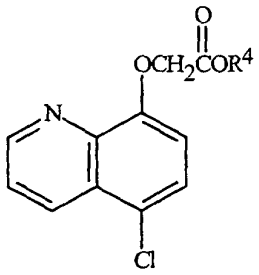
IIb

or an agriculturally useful salt thereof

wherein

R^2 is H, C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio; and

R^3 is H, C_1–C_8 alkyl, C_1–C_8 haloalkyl, C_2–C_8 alkoxyalkyl or C_1–C_6 hydroxyalkyl; and



IIc

or an agriculturally useful salt thereof

wherein

R^4 is H, C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio.

This invention also relates to herbicidal compositions comprising effective amounts of the aforesaid mixtures and at least one of the following: surfactant, solid or liquid diluent. This invention also relates to a method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation herbicidally effective amounts of the aforesaid mixtures.

In the above recitations, the term "alkyl", used either alone or in compound words such as "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl and the different butyl isomers. "Alkoxy" includes, for example, methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy isomers. The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. The total number of carbon atoms in a substituent group is indicated by the "C_i–C_j" prefix where i and j are numbers from 1 to 12.

Some of the compounds of Formulae **IIa**, **IIb** and **IIc** can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

Some of the compounds of Formulae **Ia** and **Ib** and Formulae **IIa**, **IIb** and **IIc** can be present in the form of salts. In view of the close relationship between these compounds in their free forms and their agriculturally useful salts, including their equilibration under

physiological and environmental conditions, hereinbefore and hereinafter any reference to Formulae **Ia** and **Ib** and Formulae **IIa**, **IIb** and **IIc** is to be understood as including both the free compounds and their agriculturally useful salts, where appropriate and expedient.

The salts of the compounds of Formulae **Ia** and **Ib** and Formulae **IIa**, **IIb** and **IIc** include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds of Formulae **Ia** and **Ib** and Formulae **IIa**, **IIb** and **IIc** also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine) or inorganic bases (e.g., hydrides, hydroxides, or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a carboxylic acid or enol. Preferred salts include the lithium, sodium, potassium, triethylammonium, and quaternary ammonium salts.

Preferred for reasons of better weed control or improved crop safety are mixtures of the invention comprising:

(1) the compound of Formula **Ia** and a compound selected from the compounds of Formula **IIa**, Formula **IIb** and Formula **IIc**; and

(2) the compound of Formula **Ib** and a compound selected from the compounds of Formula **IIa**, Formula **IIb** and Formula **IIc**.

Most preferred for reasons of better weed control or improved crop safety are:

(1a) the mixture of Preferred (1) comprising the compound of Formula **Ia** and the compound of Formula **IIa** where R^1 is CH_2CH_3, which is ethyl 1-(2,4-dichlorophenyl)-5-(trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate (fenchlorazole-ethyl);

(1b) the mixture of Preferred (1) comprising the compound of Formula **Ia** and the compound of Formula **IIb** where R^2 and R^3 are each CH_2CH_3, which is diethyl 1-(2,4-dichlorophenyl)-4,5-dihydro-5-methyl-1*H*-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl);

(1c) the mixture of Preferred (1) comprising the compound of Formula **Ia** and the compound of Formula **IIc** where R^4 is $CH(CH_3)(CH_2)_4CH_3$, which is 1-methylhexyl [(5-chloro-8-quinolinyl)oxy]acetate (cloquintocet-mexyl);

(2a) the mixture of Preferred (2) comprising the compound of Formula **Ib** and the compound of Formula **IIa** where R^1 is CH_2CH_3, which is ethyl 1-(2,4-dichlorophenyl)-5-(trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate (fenchlorazole-ethyl);

(2b) the mixture of Preferred (2) comprising the compound of Formula **Ib** and the compound of Formula **IIb** where R^2 and R^3 are each CH_2CH_3, which is diethyl

1-(2,4-dichlorophenyl)-4,5-dihydro-5-methyl-1*H*-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl); and

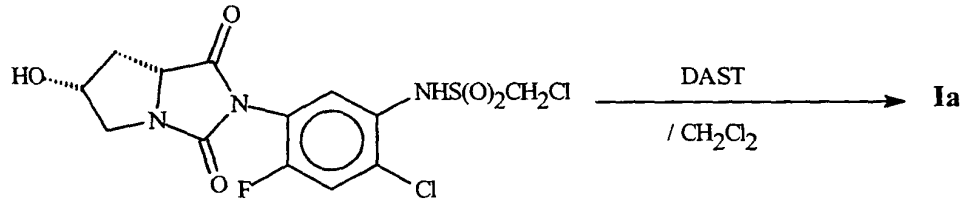
(2c) the mixture of Preferred (2) comprising the compound of Formula **Ib** and the compound of Formula **IIc** where R^4 is $CH(CH_3)(CH_2)_4CH_3$, which is 1-methylhexyl [(5-chloro-8-quinolinyl)oxy]acetate (cloquintocet-mexyl).

Also preferred are herbicidal compositions comprising aforesaid preferred mixtures and at least one of the following: surfactant, solid or liquid diluent. Further preferred embodiments are methods of controlling undesired vegetation comprising applying to the locus of the vegetation herbicidally effective amounts of the aforesaid preferred mixtures and preferred herbicidal compositions.

The preferred crops for application of the mixtures of the invention are cool-season cereals including wheat, barley, oats and rye. Wheat and barley are particularly preferred crops.

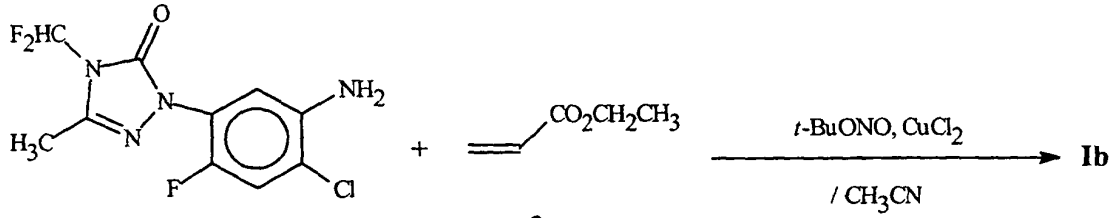
DETAILS OF THE INVENTION

The Formula **Ia** compound can be prepared as described in PCT publication WO 97/15576. The synthesis involves the reaction of the hydroxy compound of Formula **1** with diethylaminosulfur trifluoride (DAST) in dichloromethane solution.



1

The Formula **Ib** compound can be prepared as described in U.S. 5,125,958. The synthesis involves coupling of the aniline of Formula **2** with ethyl acrylate (**3**) under diazotization conditions involving *tert*-butyl nitrite and copper(II) chloride in acetonitrile.



2 **3**

Safeners of Formula **IIa** and their agriculturally useful salts can be prepared as described in U.S. 4,639,266. Safeners of Formula **IIb** and their agriculturally useful salts can be prepared by methods described in WO 91/07874. Safeners of Formula **IIc** and their agriculturally useful salts can be prepared by methods described in U.S. 4,881,966.

Combinations of the Formula **Ia** herbicide (Compound 1) and the Formula **Ib** herbicide (Compound 2) with the particular safeners of Formulae **IIa**, **IIb** and **IIc** identified in Index Table A are illustrative of the scope of this invention.

Index Table A

Safeners

Safener	Formula	R^1	R^2	R^3	R^4
1	**IIa**	H	–	–	–
2	**IIa**	CH_2CH_3	–	–	–
3	**IIb**	–	H	H	–
4	**IIb**	–	CH_2CH_3	H	–
5	**IIb**	–	H	CH_2CH_3	–
6	**IIb**	–	CH_2CH_3	CH_2CH_3	–
7	**IIc**	–	–	–	H
8	**IIc**	–	–	–	$CH(CH_3)(CH_2)_4CH_3$

These combinations thus include those listed in the following Mixture Table A.

Mixture Table A

Compound	Safener	Compound	Safener	Compound	Safener
1	1	1	7	2	5
1	2	1	8	2	6
1	3	2	1	2	7
1	4	2	2	2	8
1	5	2	3		
1	6	2	4		

In Mixture Table A, the ratio of the herbicidal compound of Formula **Ia** (Compound 1) to each safener of Formulae **IIa**, **IIb** or **IIc** (Safeners 1–8) are in general 10:1 to 1:10 by weight, with weight ratios of 4:1 to 1:4 preferred for most uses. The ratio of the herbicidal compound of Formula **Ib** (Compound 2) to each safener of Formulae **IIa**, **IIb** or **IIc** (Safeners 1–8) are in general 10:1 to 1:10 by weight, with weight ratios of 4:1 to 1:4 preferred for most uses.

Formulation

The mixtures of at least one compound of Formulae **Ia** and **Ib** with the Formulae **IIa**, **IIb** or **IIc** compounds can be formulated in a number of ways:

(a) the Formulae **Ia** and/or **Ib** and Formulae **IIa**, **IIb** or **IIc** compounds can be formulated separately and applied separately, with preferably the Formulae **IIa**, **IIb** or **IIc** safeners applied first; or

(b) more preferably the Formulae **Ia** and/or **Ib** and Formulae **IIa**, **IIb** or **IIc** compounds can be applied simultaneously in an appropriate weight ratio, e.g., as a tank mix; or

(c) most preferably the Formulae **Ia** and/or **Ib** and Formulae **IIa**, **IIb** or **IIc** compounds can be formulated together in the proper weight ratio.

Mixtures of at least one compound of Formulae **Ia** and **Ib** with the Formulae **IIa**, **IIb** or **IIc** compounds will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent and/or a surfactant wherein the formulation is consistent with the physical properties of the active ingredients, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including micro-emulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. Active ingredients can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredients. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredients, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5–90	0–94	1–15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5–50	40–95	0–15
Dusts	1–25	70–99	0–5
Granules and Pellets	0.01–99	5–99.99	0–15
High Strength Compositions	90–99	0–10	0–2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillinite, attapulgite and kaolin, starch, sugar, silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkylnaphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147–48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8–57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

For further information regarding formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10–41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138–140, 162–164, 166, 167 and 169–182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1–4;

Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81–96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound 1 is the compound of Formula **Ia**, which is (6*S-cis*)-1-chloro-*N*-[2-chloro-4-fluoro-5-(6-fluorotetrahydro-1,3-dioxo-1*H*-pyrrolo-[1,2-*c*]imidazol-2(3*H*)-yl)phenyl]methanesulfonamide, and Compound 2 is the compound of Formula **Ib**, which is ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate (carfentrazone-ethyl). Safener numbers are defined in Index Table A (page 6).

Example A

High Strength Concentrate	
Compound 1	9.0%
Safener 2	89.5%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%.

Example B

Wettable Powder	
Compound 1	52.0%
Safener 6	13.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example C

Granule	
Compound 1	5.0%
Safener 8	5.0%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%.

Example D

Aqueous Suspension

Compound 1	5.0%
Safener 8	20.0%
hydrated attapulgite	3.0%
crude calcium ligninsulfonate	10.0%
sodium dihydrogen phosphate	0.5%
water	61.5%.

Example E

Extruded Pellet

Compound 1	2.3%
Safener 8	22.7%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example F

High Strength Concentrate

Compound 2	9.0%
Safener 2	89.5%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%.

Example G

Wettable Powder

Compound 2	52.0%
Safener 6	13.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example H

High Strength Concentrate

Compound 2	49.2%
Safener 8	49.3%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%.

Utility

Test results indicate that combinations of the chlorofluorobenzene herbicides of Formulae **Ia** and/or **Ib** with a safener of Formulae **IIa**, **IIb** or **IIc** affords highly active herbicidal mixtures, providing unexpected safening on cool-season cereal crops such as wheat, barley and rye, while retaining good efficacy for controlling many problem weeds in these crops. Certain combinations even show a greater-than-additive or synergistic effect on selected weeds.

Herbicidally effective amounts of the compounds of Formulae **Ia** and/or **Ib** and antidotally effective amounts of the safeners of Formulae **IIa**, **IIb** or **IIc** will vary depending on environmental conditions, formulation, method of application, amount and type of vegetation present, etc. The use rate ratios of Formula **Ia** to Formulae **IIa**, **IIb** or **IIc** are in general 10:1 to 1:10 by weight, with weight ratios of 4:1 to 1:4 preferred for most uses. The use rate ratios of Formula **Ib** to Formulae **IIa**, **IIb** or **IIc** are in general 10:1 to 1:10 by weight, with weight ratios of 4:1 to 1:4 preferred for most uses. In general, the Formula **Ia** compound is applied at a rate from 1 to 100 g ai/ha, and preferably the Formula **Ia** compound is applied at a rate from 2 to 20 g ai/ha. In general, the Formula **Ib** compound is applied at a rate from 1 to 100 g ai/ha, and preferably the Formula **Ib** compound is applied at a rate from 8 to 40 g ai/ha. In general, the Formulae **IIa**, **IIb** or **IIc** compounds are applied at rates from 0.1 to 1000 g ai/ha, and preferably the Formulae **IIa**, **IIb** or **IIc** compounds are applied at rates from 0.5 to 120 g ai/ha.

For selective control of certain weed species in cereal crops, the mixtures of the invention are best applied when the cereal plants are at about the 1-leaf through tillering stage and the weed plants are correspondingly young. One skilled in the art can readily determine application rates and ratios of the herbicides of Formulae **Ia** and/or **Ib** to the safeners of Formulae **IIa**, **IIb** or **IIc** as well as timing necessary for the desired level of weed control and crop safety.

The Formulae **Ia** and/or **Ib** and Formulae **IIa**, **IIb** or **IIc** mixtures of this invention can additionally be used in combination with other commercial herbicides, insecticides or fungicides. A mixture of one or more of the following herbicides with the Formulae **Ia** and/or **Ib** and Formulae **IIa**, **IIb** or **IIc** mixtures of this invention may be particularly useful

for weed control. Examples of other herbicides particularly useful as mixture partners are: 2,4-D, bentazon, benzoylpropethyl, bromoxynil, chlorsulfuron, chlortoluron, clodinafop, clopyralid, cyanazine, diallate, dicamba, diclofop, difenzoquat, diflufenican, fenchlorazole, fenoxaprop, flamprop-M-isopropyl, fluroglycophen-ethyl, fluroxypyr, glyphosate, imazamethabenz, ioxynil, isoproturon, linuron, MCPA, mecoprop, methabenzthiazuron, metosulam, metoxuron, metribuzin, metsulfuron methyl, *N*-[[(4,6-methoxy-2-pyrimidinyl)-amino]carbonyl]-2-(ethylsulfonyl)imidazo[1,2-a]pyridine-3-sulfonamide (ISO-proposed: sulfosulfuron), neburon, paraquat, pendimethalin, propanil, prosulfocarb, prosulfuron, quinclorac, simazine, terbutryn, thifensulfuron methyl, tralkoxydim, triallate, triasulfuron, tribenuron methyl and trifluralin.

In certain instances, combinations with other herbicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

The following data demonstrate the surprising safening of the mixtures of this invention on cool-season cereal crops while retaining excellent efficacy against many weeds. The weed control afforded by the mixtures of this invention are not limited, however, to these species. Compound 1 is the compound of Formula **Ia**, which is (6*S*-*cis*)-1-chloro-*N*-[2-chloro-4-fluoro-5-(6-fluorotetrahydro-1,3-dioxo-1*H*-pyrrolo[1,2-*c*]imidazol-2(3*H*)-yl)phenyl]methanesulfonamide, and Compound 2 is the compound of Formula **Ib**, which is ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate (carfentrazone-ethyl). Safener numbers are defined in Index Table A (page 6).

TEST A

Test Protocol

The crops: winter wheat (*Triticum aestivum*, TRZAW), spring wheat (*Triticum aestivum*, TRZAS) and spring barley (*Hordeum vulgare*, HORVS); and the weeds: pigweed (*Amaranthus retroflexus*, AMARE), common lambsquarters (*Chenopodium album*, CHEAL), cleavers (*Galium aperine*, GALAP), kochia (*Kochia scoparia*, KCHSC), henbit (*Lamium amplexicaule*, LAMAM), scentless chamomile (*Matricaria inodora*, MATIN), wild buckwheat (*Polygonum convolvulus*, POLCO), Russian thistle (*Salsola kali*, SASKR), wild mustard (*Sinapsis arvensis*, SINAR), black nightshade (*Solanum nigrum*, SOLNI) and common chickweed (*Stellaria media*, STEME) were planted in a sterilized growing medium at the depths indicated and grown in a greenhouse approximately 10–17 days to the stages shown:

Species	Depth (cm)	Growth Stage	Species	Depth (cm)	Growth Stage
winter wheat	2.5	1–2 leaf	*L. amplexicaule*	0.4	1–2 leaf pair
spring wheat	2.5	1–2 leaf	*M. inodora*	0.4	2–4 leaf
spring barley	2.5	1–2 leaf	*P. convolvulus*	1.2	1–2 leaf
A. retroflexus	0.4	1–2 leaf	*S. kali*	1.8	2–4 leaf
C. album	0.5	2–4 leaf	*S. arvensis*	1.2	2–3 leaf
G. aparine	1.2	2–3 whorl	*S. nigrum*	1.8	1 leaf
K. scoparia	0.4	4–8 leaf	*S. media*	0.4	2–3 leaf pair

The pots were irrigated as needed with water containing 200 ppm N from 20-20-20 fertilizer. The greenhouse was maintained at approximately 21–24 °C during the day and 13–16 °C at night with 14 hours of daylight supplemented as needed by metal halide lamps.

Compound 1 was applied at 8 g ai/ha postemergence alone and in combination with 1, 2 and 4 g ai/ha of Safener 2, Safener 6 or Safener 8. All samples were sprayed in a non-phytotoxic solvent in a volume of 309 L/ha. Assessments of crop response and weed control were made by visual inspection 14 days following application. A visual rating system was used based on a percentage scale from 0 to 100%, relative to adjacent untreated control plants. On this scale 0% represents no visual differences relative to an untreated control, and 100% represents complete kill of the given crop or weed species.

Table A represents visual assessments of crop response and specific weed control with Compound 1 applied alone and in combination with Safener 2, Safener 6 or Safener 8. Different ratios of Compound 1 to Safener 2, ratios of Compound 1 to Safener 6, ratios of Compound 1 to Safener 8, and different formulation types, also provide useful crop safening and weed control from the combinations.

TABLE A

Effect of Compound 1 and as Active Ingredient Alone and in Mixtures with Safeners 2, 6 and 8

Application Rates (g ai/ha)		Crops			Weeds				
		TRZAW	TRZAS	HORVS	AMARE	CHEAL	GALAP	KCHSC	LAMAM
Compound 1	Safener								
Compound 1 Alone									
8	–	10	10	10	100	100	80	100	65
With Safener 2									
8	1	5	5	5	100	100	90	100	65
8	2	5	5	10	100	100	100	100	80
8	4	5	5	2	100	100	100	100	60
With Safener 6									
8	1	5	5	5	100	100	85	100	85
8	2	2	5	5	100	100	80	100	85
8	4	2	5	5	100	100	98	100	65
With Safener 8									
8	1	2	5	5	100	100	100	100	70
8	2	2	5	5	100	100	100	100	65
8	4	2	5	2	100	100	100	100	65

TABLE A continued

Application Rates (g ai/ha)		Weeds					
Compound 1	Safener	MATIN	POLCO	SASKR	SINAR	SOLNI	STEME
Compound 1 Alone							
8	–	100	100	100	100	100	80
With Safener 2							
8	1	100	100	100	100	100	100
8	2	100	100	100	85	100	100
8	4	100	100	100	100	100	100
With Safener 6							
8	1	100	100	100	100	100	100
8	2	100	100	100	100	100	100
8	4	100	100	100	100	100	100
With Safener 8							
8	1	100	100	100	100	100	100
8	2	100	100	100	100	100	100
8	4	100	100	100	100	100	100

As can be seen from Table A, mixtures of Compound 1 with Safener 2, Safener 6 or Safener 8 were found to cause significantly less injury to the wheat and barley compared to Compound 1 applied alone. Compound 1 alone and in combination with Safener 2, Safener 6 or Safener 8 gave 100% control of most weed species. In this test, combinations of Compound 1 with Safener 2 or Safener 8 appeared to increase control of *Galium aparine*. The surprising combination of crop safening and excellent weed control make these mixtures particularly commercially valuable.

TEST B

Test Protocol

The crops: winter wheat (*Triticum aestivum*, TRZAW), spring wheat (*Triticum aestivum*, TRZAS), winter barley (*Hordeum vulgare*, HORVW) and spring barley (*Hordeum vulgare*, HORVS); and the weeds: common lambsquarters (*Chenopodium album*, CHEAL), cleavers (*Galium aperine*, GALAP), henbit (*Lamium amplexicaule*, LAMAM), wild

buckwheat (*Polygonum convolvulus*, POLCO), Russian thistle (*Salsola kali*, SASKR), and black nightshade (*Solanum nigrum*, SOLNI) were planted in a sterilized growing medium at the depths indicated and grown in a greenhouse approximately 10–17 days to the stages shown:

Species	Depth (cm)	Growth Stage	Species	Depth (cm)	Growth Stage
winter wheat	2.5	1–2 leaf	*G. aparine*	1.2	2–3 whorl
spring wheat	2.5	1–2 leaf	*L. amplexicaule*	0.4	1–2 leaf pair
winter barley	2.5	1–2 leaf	*P. convolvulus*	1.2	1–2 leaf
spring barley	2.5	1–2 leaf	*S. kali*	1.8	2–4 leaf
C. album	0.5	2–4 leaf	*S. nigrum*	1.8	1 leaf

The pots were irrigated as needed with water containing 200 ppm N from 20-20-20 fertilizer. The greenhouse was maintained at approximately 21–24 °C during the day and 13–16 °C at night with 14 hours of daylight supplemented as needed by metal halide lamps.

Test B was comprised of six replicates. Compound 2 was applied at 16 g ai/ha postemergence alone and in combination 8 g ai/ha of Safener 2, Safener 6 or Safener 8. All samples were sprayed in a non-phytotoxic solvent in a volume of 309 L/ha. Assessments of crop response and weed control were made by visual inspection 5 days following application. A visual rating system was used based on a percentage scale from 0 to 100%, relative to adjacent untreated control plants. On this scale 0% represents no visual differences relative to an untreated control, and 100% represents complete kill of the given crop or weed species.

Table B represents mean visual assessments of crop response and specific weed control with Compound 2 applied alone and in combination with Safener 2, Safener 6 or Safener 8. Different ratios of Compound 2 to Safener 2, ratios of Compound 2 to Safener 6, ratios of Compound 2 to Safener 8, and different formulation types, also provide useful crop safening and weed control from the combinations.

TABLE B

Mean* Effect of Compound 2 and as Active Ingredient Alone and in Mixtures with Safeners 2, 6 and 8

Application Rates (g ai/ha)		Crops				Weeds				
		HORVW	TRZAW	TRZAS	HORVS	GALAP	LAMAM	SASAKR	SOLNI	POLCO
Compound 2	Safener									
Compound 2 alone										
16	–	9	9	22	8	100	100	100	100	100
With Safener 2										
16	8	8	6	13	3	99	100	98	100	100
With Safener 6										
16	8	6	4	5	2	100	100	99	100	100
With Safener 8										
16	8	4	4	8	3	100	100	100	100	100

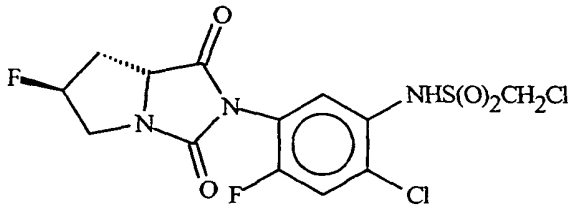
* Values are the mean response of six replicates.

As can be seen from Table B, mixtures of Compound 2 with Safener 2, Safener 6 or Safener 8 were found to cause significantly less injury to wheat and barley compared to Compound 2 applied alone. Compound 2 alone and in combination with Safener 2, Safener 6 or Safener 8 gave 98–100% control of the weed species. The surprising combination of crop safening and excellent weed control make these mixtures particularly commercially valuable.

CLAIMS

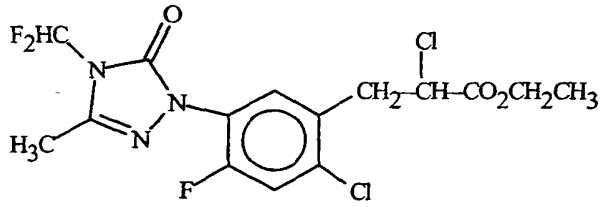
What is claimed is:

1. A mixture comprising a herbicidally effective amount of at least one herbicidal compound selected from the group consisting of:



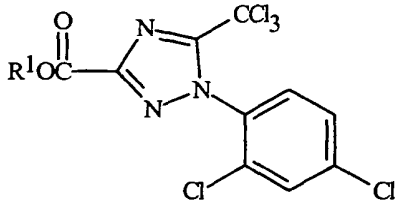
Ia

which is (6*S*-*cis*)-1-chloro-*N*-[2-chloro-4-fluoro-5-(6-fluorotetrahydro-1,3-dioxo-1*H*-pyrrolo-[1,2-*c*]imidazol-2(3*H*)-yl)phenyl]methanesulfonamide,
or an agriculturally useful salt thereof; and



Ib

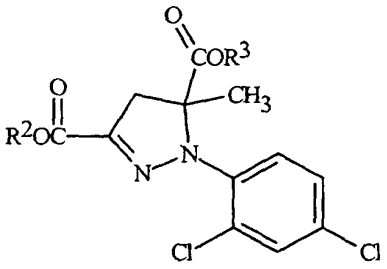
which is ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate,
or an agriculturally useful salt thereof;
in combination with an antidotally effective amount of a safener compound selected from the group consisting of:



IIa

or an agriculturally useful salt thereof
wherein

R^1 is C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio;



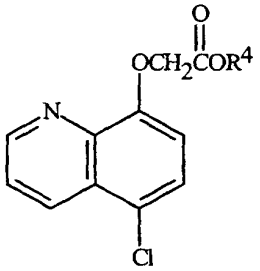
IIb

or an agriculturally useful salt thereof

wherein

R^2 is H, C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio; and

R^3 is H, C_1–C_8 alkyl, C_1–C_8 haloalkyl, C_2–C_8 alkoxyalkyl or C_1–C_6 hydroxyalkyl; and



IIc

or an agriculturally useful salt thereof

wherein

R^4 is H, C_1–C_{12} alkyl, C_3–C_7 cycloalkyl, C_2–C_8 alkenyl or C_2–C_8 alkynyl, each optionally substituted with at least one radical selected from the group consisting of halogen, hydroxy, C_1–C_4 alkoxy and C_1–C_4 alkylthio.

2. A mixture of Claim 1 wherein the herbicidal compound is (6*S-cis*)-1-chloro-*N*-[2-chloro-4-fluoro-5-(6-fluorotetrahydro-1,3-dioxo-1*H*-pyrrolo[1,2-*c*]imidazol-2(3*H*)-yl)phenyl]methanesulfonamide.

3. The mixture of Claim 2 wherein the safener compound is ethyl 1-(2,4-dichlorophenyl)-5-(trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate.

4. The mixture of Claim 2 wherein the safener compound is diethyl 1-(2,4-dichlorophenyl)4,5-dihydro-5-methyl-1*H*-pyrazole-3,5-dicarboxylate.

5. The mixture of Claim 2 wherein the safener compound is 1-methylhexyl [(5-chloro-8-quinolinyl)oxy]acetate.

6. A mixture of Claim 1 wherein the herbicidal compound is ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]-4-fluorobenzene-propanoate.

7. The mixture of Claim 6 wherein the safener compound is ethyl 1-(2,4-dichlorophenyl)-5-(trichloromethyl)-1*H*-1,2,4-triazole-3-carboxylate.

8. The mixture of Claim 6 wherein the safener compound is diethyl 1-(2,4-dichlorophenyl)4,5-dihydro-5-methyl-1*H*-pyrazole-3,5-dicarboxylate.

9. The mixture of Claim 6 wherein the safener compound is 1-methylhexyl [(5-chloro-8-quinolinyl)oxy]acetate.

10. An agriculturally suitable composition for controlling the growth of undesired vegetation comprising an effective amount of the mixture of any of Claims 1–9 and at least one of the following: surfactant, solid or liquid diluent.

11. A method for controlling the growth of undesired vegetation by applying to the locus of the undesired vegetation a herbicidally effective amount of the mixture of any of Claims 1–9.

12. The method of Claim 11 wherein the locus of the undesired vegetation is a crop of wheat or barley.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/10359

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N43/90 A01N43/653 //(A01N43/90,43:653,43:56,43:42), (A01N43/653,43:653,43:56,43:42)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 11574 A (CIBA GEIGY AG ;GLOCK JUTTA (CH); HUDETZ MANFRED (US); KERBER ELMAR) 25 April 1996 (1996-04-25) see page 1, par. 3 and 4, and safeners (IIa), (IIb) and (IIb1) (Tables 16 - 18). ---	1-12
A	EP 0 492 367 A (HOECHST AG) 1 July 1992 (1992-07-01) page 6, line 15 - page 8, line 57 ---	1-12
A	WO 91 07874 A (HOECHST AG) 13 June 1991 (1991-06-13) cited in the application page 6, line 32 - page 7, line 6 -----	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 September 1999	15/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Klaver, J

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/10359

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